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16. ABSTRACT

A new method is presented for the determination of phosphorus in gasoline using flameless atomic absorption. Lanthanum nitrate solution is inserted in a graphite furnace prior to direct addition of gasoline. The organic matrix is charred prior to atomization of the phosphorus. The sensitivity of this method is 20 ng of phosphorus per 90-μL aliquot of gasoline. Repeated analysis of NBS triphenyl phosphate standard at the 80-ng level resulted in 2% relative standard deviation. Each determination requires less than 2 min.

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Direct Determination of Phosphorus in Gasoline by Flameless Atomic Absorption Spectrometry

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A new method is presented for the determination of phosphorus in gasoline using flameless atomic absorption. Lanthanum nitrate solution is inserted in a graphite furnace prior to direct addition of gasoline. The organic matrix is charred prior to atomization of the phosphorus. The sensitivity of this method is 20 ng of phosphorus per 90-μL aliquot of gasoline. Repeated analysis of NBS triphenyl phosphate standard at the 80-ng level resulted in 2% relative standard deviation. Each determination requires less than 2 min.

Organophosphorus compounds were originally added to gasoline as detergents to prevent fouling of spark plugs. The Clean Air Act of 1970 (*1*) limited phosphorus compounds in gasoline to 0.005 g/gal because of adverse effects to catalytic converters.

In support of this legislation, the Environmental Protection Agency (EPA) Fuels Laboratory analyzes gasoline for phosphorus. The procedure used is the molybdate–hydrazine method (*2*). It is a time-consuming colorimetric wet chemistry test. To minimize analysis time, the graphite furnace was adapted for a screening test for the direct determination of phosphorus in gasoline.

Previous studies dealing with flameless atomic absorption (AA) determination of elements in petroleum described conversion of the organic matrix to the aqueous phase prior to analysis (*3*). Limited tests were made on the effect of organic matrices on flameless AA analysis (*4*). However, no direct analytical method for phosphorus in gasoline using the graphite furnace has been reported.

EXPERIMENTAL

Instrumentation. The following Perkin-Elmer equipment was used in this investigation: A model 403 double beam atomic absorption spectrophotometer equipped with a deuterium background corrector and a phosphorus electrodeless discharge lamp (EDL), an HGA 2100 Graphite Furnace, a model 56 recorder,

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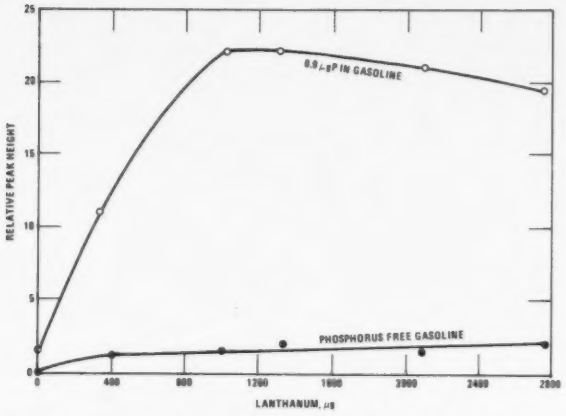

Figure 1. Effect of lanthanum on phosphorus signal response

and an M-2 calculating integrator.

Direct Injection Experiments. NBS grade triphenyl phosphate (TPP) is dissolved in phosphorus-free gasoline. The standard solutions range in concentration from 0.001 g/gal to 0.010 g/gal phosphorus.

The effect of lanthanum on phosphorus signal response is illustrated in Figure 1. Ten μL aliquots of various concentrations of lanthanum nitrate dissolved in 25% EtOH were injected into the furnace. The volume of both the phosphorus-free gasoline and the 0.9-μg phosphorus standard was held constant at 90 μL. As can be seen, concentrations in excess of 2 mg lanthanum do not appreciably interfere with absorption in the EDL beam. Maximum phosphorus signal response occurs when 960 μg of lanthanum is present in the graphite tube. Ten μL of a 15% lanthanum nitrate solution in 25% EtOH (960 μg lanthanum) is injected into the graphite furnace ahead of 90 μL of sample or standard. This amount of lanthanum enables us to achieve a lower detection limit of 0.001 g/gal (20 ng). Lower detection limits can be achieved by reducing the volume of the gasoline sample prior to injection. A stream of clean air is bubbled through a sample of gasoline. Within 15–30 min, the volume of the sample can be reduced by 50%. A 90-μL sample of 0.004 g/gal phosphorus (80 ng) standard will produce a peak height of 3.0 before concentration. After reduction in volume, the above standard will produce a peak height of 6.0.

Three purge gases were evaluated for their response to concentrations of phosphorus ranging from 20–200 ng. Helium, the lowest molecular weight purge gas used resulted in no response over the entire range of phosphorus standards. At a concentration of 200 ng phosphorus, nitrogen yielded a relative area count of 300 while argon produced a relative area count of 1000. Therefore argon was chosen as the optimum purge gas.

The method of Manning (5) was used to pyrolytically coat the interior of graphite tubes. Using this technique, we deposited an average of 112 mg of pyrolytic carbon onto each tube. However peak heights of 50% less were obtained using pyrolytically coated tubes rather than uncoated tubes.

Final Procedure. Table I outlines the operating conditions for the direct injection method. Due to the refractory nature of phosphorus, the charring cycle can be operated at 1600 °C. The interrupt gas flow mode is used for purge gas operation. In this manner of operation, the purge gas flow ceases during the atomization cycle; therefore the phosphorus is retained longer in the EDL beam, thereby increasing sensitivity.

When the phosphorus content of a sample is above 0.01 g/gal the atomization time should be increased to 15 s. This will atomize the phosphorus quantitatively off the graphite tube and result in better signal precision. The 4.0 nm bandwidth lowers the background noise to 0.5 of a scale division, thereby allowing a signal of 1.0% scale deflection to become the minimum detection limit.

The operator procedure for direct injection follows. A graphite tube which has been thermally conditioned for 15 s is injected with 10 μL of 15% lanthanum nitrate. This injection is followed by an injection of 90 μL of sample or standard. The temperature program is initiated and the phosphorus signal is analyzed in terms of absorbance at the moment of atomization. The absorbance signal is displayed on a recorder as peak height. Each tube may be used for two standards and 10 analyses. The lowering of the signal response to the standard necessitates the replacement of the graphite tube.

Table I.
INSTRUMENT OPERATING PARAMETERS

DRY CYCLE	60 SEC @ 110°C
CHAR CYCLE	50 SEC @ 1600°C
ATOMIZING CYCLE	5 SEC @ 2700°C
WAVELENGTH	214.2 nm, DEUTERIUM CORRECTION USED
BANDWIDTH	4.0 nm
PURGE GAS	ARGON, INTERRUPT MODE
REAGENT	15% LANTHANUM NITRATE IN 25% AQUEOUS ETOH
REAGENT VOLUME	10 μl ADDED FIRST
SAMPLE	90 μl

RESULTS AND DISCUSSION

The early developmental work performed in this laboratory on the phosphorus method utilized aqueous standards of potassium phosphate. Initially the phosphorus solutions analyzed in the graphite furnace yielded low signal responses. The signals were enhanced by the injection of 20 μL of 5% lanthanum nitrate. In the subsequent direct injection approach, the volume of lanthanum nitrate was reduced to 10 μL and the concentration of lanthanum nitrate was increased to 15%. The reduction in the volume of lanthanum nitrate allowed us to increase the sample size from 80 to 90 μL thereby increasing sensitivity. Runnels et al. (6) pretreated graphite tubes with lanthanum chloride and determined that 600 μg of lanthanum yielded the maximum signal in the determination of beryllium in petroleum. Our experimental data show measurably increased phosphorus signal response is obtained when 960 μg of lanthanum (10 μL of 15% lanthanum nitrate) are added to the graphite tube before addition of the standard or sample. The mechanism by which lanthanum enhances the phosphorus signal is unknown. However, the enhancement effect must be cancelled by the atomization process since the lanthanum must be replenished before each analysis.

The reduced sensitivity obtained by using pyrolytically coated tubes was most surprising since other investigators (7) using coated tubes reported a fivefold increase in sensitivity in the determination of refractory elements, other than phosphorus. We determined that the only conditioning of the graphite tube necessary is a 15-s high temperature purge.

Because of the low surface tension of organic liquids, a loss of gasoline from the micropipet tip can occur when transfering the sample to the furnace. This can result in poor reproducibility. Other investigators (3) have improved precision by chemically pretreating the disposable pipet tips before usage. Instead of chemical pretreatment, we wet the micropipet tip with gasoline sample prior to injection. This technique enables us to achieve a precision of 2.0%. The relative standard deviation is calculated from 10 injections each of 90 μL of 80 ng of TPP phosphorus standard in gasoline.

Earlier flameless AA determination of elements in gasoline was accomplished by elimination of the organic matrix. Kaegler dry ashed 1-g samples of gasoline prior to determination (3). Beaty wet ashed gasoline to extract phosphorus into the aqueous phase prior to determination in the graphite furnace (8). Similar experiments in this laboratory involved acid extraction of phosphorus from gasoline and ashing of gasoline on metal oxides. Results were variable and the procedure was time-consuming. Therefore experiments in-

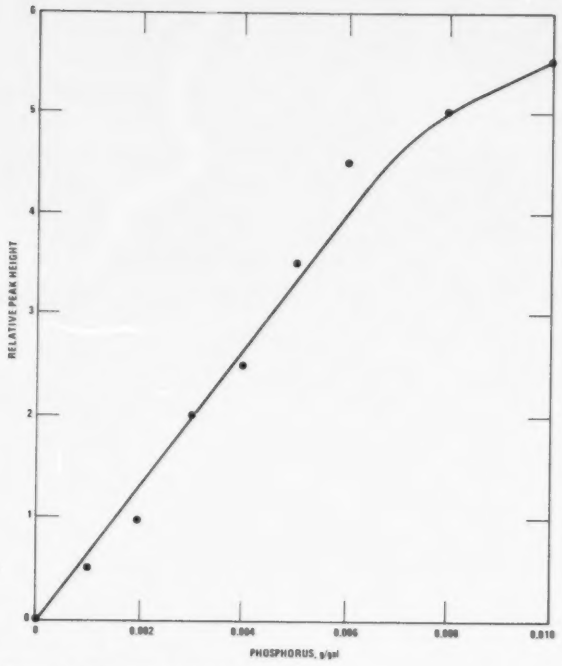

Figure 2. Response curve

volving direct injection of gasoline into the furnace were undertaken.

Figure 2 shows the phosphorus response curve for 90-μL aliquots of gasoline injected directly into the graphite furnace. Each injection is preceded by the injection of 10 μL of 15% lanthanum nitrate in 25% EtOH (960 μg lanthanum). The response is linear in the region of 0.001 g/gal (20 ng) to 0.006 g/gal (120 ng).

Phosphorus can be detected in the graphite furnace to a lower detection limit of 0.001 g/gal using 90 μL of sample. Still lower concentrations of phosphorus can be detected by concentrating the sample prior to analysis as described previously. The lower detection limit of the molybdate–hydrazine method is 0.004 g/gal (80 ng) using 3 mL of gasoline.

During the development of the method for determination of gasoline phosphorus by direct injection, 500 samples were comparatively tested by both the graphite furnace and the molybdate–hydrazine procedures. The latter method is a lengthy procedure involving burning the sample off, burning carbon off in the muffle furnace, acid digestion, and further heating and cooling. The average time required to process an individual sample in this manner is 20 min. By contrast, the graphite furnace method can process a sample in less than 2 min.

Equipment costs between the two methods are comparable if the laboratory already possess an AA equipped with a graphite furnace. The cost per graphite tube is $6.00 making the cost per replicate $0.60. Increased analytical capability and decreased personnel time per analysis are added benefits.

Further work using the direct injection of gasoline into the graphite furnace will be done. The techniques described here should be applicable to other trace elements in gasoline.

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